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(54) Title: AQUEOUS ANIONIC POLYURETHANE DISPERSIONS

(57) Abstract

Improved aqueous anionic polyurethane dispersions with a high crystallization rate, low heat activation temperature, high green strength, stability at low pH, which show good compatibility with other water based polymers and with crosslinkers. The aqueous anionic polyurethane dispersions have high heat resistance after curing or blending with a crosslinker.

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AQUEOUS ANIONIC POLYURETHANE DISPERSIONS

Background of the Invention

This invention relates to new aqueous polyurethane dispersions having high crystallization rates, good stability at low pH and high heat resistance. These are important basic properties for improved polyurethane dispersions, particularly for adhesive applications.

Description of the Prior Art

A. Sulfonated aqueous polyurethane dispersions

Wolfgang Keberle and Dieter Dieterich, Canadian Pat. 764,009 (July 25, 1967) disclose aqueous polyurethane dispersions prepared from hydroxy-and carboxy-sulphonic acids, aminosulphonic acids, and the hydroxy, mercapto-and amino-carboxylic and sulphonic acids, polycarboxylic and polysulphonic acids include also the addition products (which may be saponified) of unsaturated acids and unsaturated nitriles, of cyclic dicarboxylic acid anhydrides, of sulphocarboxylic acid anhydrides, the addition products of reaction products of olefines with sulphur trioxide such as carbyl sulphate, of epoxypropane-sulphonic acid of sultones such 1,3-propanesultone, 1,4-butanesultone, 1,8-naphthosultone, of disulphonic acid anhydrides to aliphatic and aromatic amines.

Dieter Dieterich and Otto Bayer, U.S.Pat. 3,479,310 (Nov. 18, 1969) disclose aqueous polyurethane dispersions based on hydroxy-and carboxy-sulphonic acids, and aminosulphonic acids as described in Canadian Patent 764,009.

Hans Ludwig Honig, Gerhard Balle, Wolfgang Keberle, and Dieter Dieterich, U.S. Pat. 3,705,164 (Dec.5, 1972) disclose sulfonated aqueous polyurethane dispersions based on mixtures of ethylenediamine and 1,3-propane sultone.

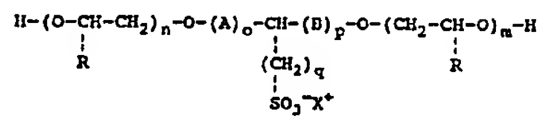
Dieter Lesch and Wolfgang Keberle, Canadian Pat. 928323 (June 12, 1973) disclose sulfonated aqueous polyurethane dispersions based on the sodium salt of N-(2-aminoethyl)-2-aminoethanesulphonic acid. The patent also relates to a process for preparation of the diamine sulfonate.

It was mentioned in this patent that Belgian Patent Specification No. 673,432 (March,1966) to Keberle et al. discloses sulfonated aqueous polyurethane dispersions based on 2,4 diaminobenzene sulphonic acid. However, the polyurethane dispersions produced from these aromatic diaminosulphonic acids undergo discoloration on exposure to light. It was also mentioned that the process for the preparation of aliphatic diaminosulphonic acids whose salts are suitable for use as anionic structural components for light-fast polyurethane dispersions are already known, these known processes either entail considerable expenditure in apparatus or involve the use of physiologically very dangerous starting materials (reaction of sultone with amines).

Harro Witt and Dieter Dieterich, U.S. Pat. 3,870,684 (Mar. 11, 1975) disclose aqueous polyurethane dispersions based on an adduct of 1,3-propanesultone and ethylenediamine (sultone-diamine adducts are described in German Auslegeschrift No.1,200,318). It also mentioned hydroxy- and carboxy-sulphonic acids, and aminosulphonic acids which described in Canadian Patent 764,009 may be used to prepare aqueous polyurethane dispersions.

Helmut Reiff, Wolfgang Wenzel, Jurgen Grammel, and Dieter Dieterich, U.S. Pat. 4,108,814 (Aug.22, 1978), disclose aqueous polyurethane

dispersions based on sulphonate diols have the general formula:



In the examples, the following sulfonated diol and diamine were used to prepare aqueous polyurethane dispersions: (1) Sodium salt of propoxylated 3-hydroxy-2-hydroxymethyl propane-sulphonic acid-1 (molecular weight 428) (AD); and (2) Sodium salt of ethylenediamino-2-ethanesulphonic acid (AAS)

Peter H. Markusch, James W. Rosthauser, and Michael C. Beatty, U.S.Pat. 4,501,852 (Feb.26, 1985), disclose aqueous polyurethane dispersions based on 70% solution in toluene of propoxylated sodium salt of 1,4-dihydroxy-2-butane sulfonic acid having a molecular weight of 430 ("sulfonate diol").

Otto Lorenz, Helmut Reiff, and Dieter Dieterich, Europaische Pat. 0 222 289 A3 (May 21, 1987), used sodium salt of 2-aminoethyl-2 aminoethanesulfonic acid (Na-AAS) and dimethylsulfonate to prepare polyurethane dispersions.

Rudolf Hombach, and Helmut Reiff, U.S.Pat. 4,663,337 (May 5, 1987) used sodium salt of N-(aminoethyl)-aminoethane sulfonic acid to prepare polyurethane dispersions.

Wolfgang Henning, Rudolf Hombach, Walter Mechel, and Manfred Dollhausen, U.S.Pat. 4,870,129 (Sep.26, 1989), used sodium salt of N-(2-aminoethyl)-2-aminoethane sulfonate acid (AAS salt) to prepare polyurethane dispersions. The patent also states "Anionic or potentially anionic starting components include, for example, aliphatic diols containing sulphonate

groups according to DE-OS No. 2,446,440 or DE_OS No. 2,437,218, diols and/or diaminosulphonates containing carboxylate groups or groups capable of being converted into carboxylate groups as described in CA-PS 928,323, e.g. the sodium salt of N-(2-aminoethyl)-2-aminoethane sulphonic acid".

Wolfgang Henning, Harald Petersen, and Gerhard Moormann, U.S. Pat. 4,921,842 (May 1, 1990) used a propoxylated adduct of but-2-ene-1,4-diol and $NaHSO_3$ (Mw 430: 70% in toluene) to prepare polyurethane dispersions. The patent states that "the anionic synthesis components include the aliphatic diols containing sulfonate groups according to DE-OS No. 2,446,440 (U.S. Pat.No.4,108,814) or DE-OS No. 2,437,218, diols and/or diamines containing sulfonate or carboxylate groups or sulfonic or carboxylic acid groups convertible into sulfonate or carboxylate groups of the type described in CA-PS No. 928,323, such as the sodium salt of N-(2-aminoethyl)-2-aminoethane sulfonic acid".

Sven H.Ruetman and Joginder N. Anand, U.S.Pat. 4,895, 894 (Jan. 23, 1990), describe "Illustrative but non-limiting the compounds containing a potential anionic (ionic) group are ... 1,7 dihydroxynaphthalenesulfonic acid-3 (sodium salt, potassium salt, triethylammonium salt),1,8-dihydroxynaphthalenedisulfonic acid-2,4 (sodium salt, potassium salt, triethylammonium salt), 2,4 diaminotoluenesulfonic acid-5 (sodium salt, potassium salt, triethylammonium salt), the sulfonate diols described in U.S. Pat. No. 4,108,814".

Jurgen Fock and Dietmar Schedlitzki, U.S. Patent No. 5,001,189 (March 19, 1991), disclose an aqueous polyurethane dispersion based on a polyol component which is a polyoxyalkylene ether with an average molecular weight of 400 to 10,000 and having at least two terminal hydroxyl groups and at least one $-SO_3X$ group. A sulfonated polyether polyol is disclosed.

B. Polyurethane Dispersions based on Diisocyanate Mixtures

Wolfgang Henning, Rudolf Hombach, Walter Meckel, and Manfred

Dollhausen, U.S.Pat. 4,870,129 (Sep. 26, 1989), disclose polyurethane dispersions based on mixtures of hexamethylene diisocyanate with $Q(NCO)_2$ in which Q denotes a divalent aliphatic hydrocarbon group with 4-12 carbon atoms or a divalent cycloaliphatic hydrocarbon group with 6-15 carbon atoms.

Herbert Fisch and Lothar Maempel, DE 40 24 567 Al, disclose polyurethane dispersions based on mixtures of hexamethylene diisocyanate and toluene diisocyanate.

Hans Bauriedel, Wolfgang klauck, and Gunther Henke, PCT/EP92/00560 (26/11/92) (DE 40 24567 A1) and (DE 41 09 477 A1) (Sep. 24, 1992) disclose aqueous polyurethane dispersions based on mixture of tetramethylxylylene diisocyanate (TMXDI) with hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 1,3-xylylene diisocyanate (XDI), 2,2,4-trimethyl-1,6-hexane diisocyanate (TMDI), toluene diisocyanate (TDI), 4,4′-diphenylmethane-diisocyanate (MDI) and dicyclohexylmethane 4,4-diisocyanate (H_{12}MDI).

C. Crystallization of Polyurethane Dispersions

Lani S. Kangas and Charles W. Stobbie IV, European Pat. 0 344 912 A3 (06/12/1989), disclose moisture curable and hot melt polyurethane based on crystalline or semicrystalline polyester diols having melting points between 30°C and 80°C. The polyurethane composition exhibits improved crystallization rates and posses high green strength.

Palitha K. Abeywardena and Pak T. Leung, WO 92/02568 (Feb.20, 1992), disclose polyurethane dispersions based on a crystalline oligomeric or polymeric polyol.

Dispercoll KA-8464, an aqueous polyurethane dispersion product of Bayer Corporation and Miles (a Bayer USA, Inc. Company), based on HDI and IPDI has a high crystallization rate and stability at low pH levels, but has medium heat resistance. U-42, another Bayer aqueous polyurethane dispersion product has high heat resistance, but a low crystallization rate.

D. Sulfonated Anionic Polyurethane Dispersions

Helmet Reiff, Wolfgang Wenzel, Jargen GRammel and Dieter Dieterich, U.S. Pat. 4,108,814, disclose the use of sulfonate polyether diols to prepare polyurethane dispersions.

Wolfgang Henning, Rudolf Hanbach, Walter Meckel and Manfred Dollhausen, U.S. Pat. 4,870,129, disclose the use of sulfonate diamine as a chain extender in preparing polyurethane dispersions.

Summary of the Invention

This invention relates to an improved polyurethane prepolymer and aqueous polyurethane dispersions (PUDs) made therefrom, the dispersions having a high crystallization rate, good quality stability at low pH and high heat resistance. Accordingly, the invention provides aqueous anionic polyurethane dispersions made from a prepolymer which is the reaction product of a sulfonated polyester polyol and/or a sulfonated polyester polyol mixed with dimethylol propionic acid (DMPA) and/or a sulfonated polyester polyol mixed with another polyester polyol and DMPA and/or a sulfonated polyester polyol mixed with a polyether polyol and DMPA and/or a sulfonated polyester polyol mixed with another polyester polyol and a polyether polyol and DMPA, and/or mixtures of any or all of the foregoing, reacted with hexamethylene diisocyanate (HDI) or HDI mixed with tetramethylxylylene diisocyanate (TMXDI) and/or HDI mixed with an aromatic diisocyanate e.g., toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), or the like, and/or HDI mixed with other aliphatic diisocyanate e.g., isophorone diisocyanate (IPDI), dicyclohexylmethane 4,4-diisocyanate ($H_{12}MDI$), or the like.

The prepolymer is then dispersed in water with a tertiary amine e.g. triethylamine (TEA) or if made in a salt form such as a sodium salt (as exemplified in some of the Examples below) TEA is not necessary. These are

considered equivalents. The prepolymer is also chain-modified i.e., chain extended and/or chain terminated. Suitable chain extenders are: ethylenediamine or 1,4-butanediol or ureido diamine (imidazolidinone diamine) or N-isodecyloxypropyl-1,3-diaminopropane (DA-14 from Exxon). Suitable chain terminators are: taurine (2-aminoethanesulfonic acid) or its sodium salt, or ethanolamine or isethonic acid (2-hydroxyethanesulfonic acid) or its sodium salt. Mixtures of the extenders and terminators may also be used as exemplified in some of the Examples below. Chain extenders and chain terminators are herein referred to collectively as chain modifiers.

Detailed Description of the Invention

In preferred embodiments, the present invention provides aqueous anionic polyurethane dispersions with high crystallization rates, low heat activation temperature and high green strength. These aqueous anionic polyurethane dispersions are stable at low pH (e.g. 5-7). Also these aqueous polyurethane dispersions exhibit a high degree of compatibility not only with other water-based polymers (e.g. vinyl acetate emulsion), but also with crosslinking agents (e.g. Bayer/Miles' Desmodur DA). These aqueous polyurethane dispersions also have high heat resistance after curing or blending with a crosslinker.

HIGH CRYSTALLIZATION RATE POLYURETHANE DISPERSIONS

Polyurethane generally consists of a hard segment (isocyanate and chain extender) and a soft segment (polyol). European Pat. 0 344 912 A3 and WO 92/02568 disclose that the crystallization of polyurethane dispersions depends on the structure, composition and molecular weight of the polyol component. It would therefore seem from the prior art that crystallization rate does not depend on the hard segment crystallization but on the soft segment crystallization.

Unexpectedly, it has been found in the compositions of the present invention that the crystallization rate of these polyurethane dispersions depends on the structure of the diisocyanate (hard segment).

Such polyurethane dispersions according to the invention include, in some embodiments, polyester polyol, for example Rucoflex 105-55 (a hexanediol adipate polyol, Eq.wt. 996, available from Ruco Polymer Corporation), dimethylol propionic acid (DMPA), hexamethylene diisocyanate (HDI), tetramethylxylylene diisocyanate (TMXDI), Triethylamine (TEA) if not in salt form, and ethylene diamine/ethanolamine (EDA/EA). The crystallization rates of several such compositions are shown in Table 1.

Table 1. Crystallization Rate and Ratio of HDI/TMXDI

TMXDI/HDI (Molar)	DSC First Run Heat (Cal./G)	DSC Second Run Heat (Cal./G)	Cry. Rate* (%)
1/0	12.6	0	0
0.8/0.2	17.4	0.4	2.3
0.5/0.5	10.79	6.15	57.0
0.4/0.6	15.9	9.95	62.6
0.33/0.66	11.4	8.4	73.7
0/1	10.5	8.5	80.1
NP-4041 (H.B. Fuller PUD based on TMXDI and butanediol adipate polyol and EDA/EA/DETA (diethylene-driamine) chain extender	11.5	0	0
KA-8464 (Bayer/Miles PUD based on HDI/IPDI and polyester polyol)	13.7 16.5	10.1 11.4	73.7 69.1

* Crystallization rate = DSC Second Run Heat/DSC First Run Heat

DSC testing: The samples were heated from -40 to 140 degrees C at 10 degrees C/minute. The resulting thermographics are "first Run". The samples were then quench cooled and reheated at 10 degrees C/minute to produce the "Second Run" thermographics.

The crystallization rates of PUDs based only on TMXDI (e.g. NP-4041) and based only on HDI were 0 and 80%, respectively as seen in

Table 1. The crystallization rate of KA-8464 as shown in Table 1 was about 70%, close to that of a PUD based on a 2/1 molar ratio of HDI/TMXDI, but KA-8464 is based on HDI/IPDI.

From this it can be seen that aqueous polyurethane dispersions based on HDI and its mixtures with other diisocyanate may, according to the invention, be synthesized with varying crystallization rates, depending on the ratio of HDI to the other diisocyanate(s). The ratio may range from 100/0 to 0/100 by weight, preferably from 100/0 to about 50/50.

Bauriedel et al., PCT/EP92/00560 (26/11/92) (DE 40 24567 A1), disclose aqueous polyurethane dispersions based on one isocyanate component consisting of at least 20% by weight TMXDI, and other diisocyanates (HDI, IPDI, XDI, TMDI, TDI, MDI and $H_{12}MDI$). TMXDI, at least 20% by weight in its mixture with other diisocyanate(s) is used to decrease the prepolymer viscosity made from the diisocyanate mixture, so a low solvent or even a solvent free process can be used to prepare the prepolymer of the patent.

In the present invention, however, TMXDI in its mixture with HDI is used to adjust the crystallization rate of the resulting polyurethane dispersions because the amount of TMXDI used was unexpectedly found to be inversely proportional to the crystallization rate of the resulting polyurethane dispersions. The use of smaller amounts of TMXDI down to zero produces a higher crystallization rate.

It was also unexpectedly found, according to the invention, that the crystallization rate of the polyurethane dispersions of the invention also depends on the ratio of chain extender, e.g.ethylene diamine (EDA) to the chain terminator, e.g. ethanolamine (EA) used. The crystallization rate for several compositions are shown in Table 2.

Table 2. Crystallization Rate and Ratio of EDA/EA

PUD Samples	#4133-7	#4133-8	#4133-9
Rucoflex 105-55 (hexanediol adipate polyol Eq. Wt. 996)	64.38	65.59	66.41
DMPA	4.35	4.39	4.45
TEA	6.22	6.29	6.37
TMXDI	8.54	8.64	8.75
HDI	11.44	11.57	11.71
EA	4.59	2.36	0.43
EDA	0	1.16	1.88
Crystallization Rate (%)	64.64	75.96	84.18

In Table 2, PUD samples #4133-7, #4133-8 and #4133-9 have nearly same contents of DMPA, TEA, TMXDI and HDI, but different ration of EDA/EA in their compositions. These samples exhibited much different crystallization rates.

Therefore, the synthesis aqueous polyurethane dispersions with high crystallization rate depends not only on ratio of HDI to other diisocyanate, but also on ratio of chain extender to chain terminator. The ration may vary from a chain extender/chain terminator ration of 100/0 to 0/100, preferably from about 50/50 to about 100/0 by weight.

Examples of useful chain extenders include aliphatic, cycloaliphatic, and aromatic diamines, like ethylenediamine, hexamethylenediamine, 1,4-cyclohexylenediamine, piperazine, N-methylpropylenediamine, diaminophenylsulfone, diaminodiphenylether, diaminodiphenyldimethylmethane, 2,4-diamino-6-phenyltriazine, isophoronediamine, dimer fatty acid diamine, N-isodecycloxy propyl-1,3-

diaminopropane (DA-14), imidazolidinone diamine (ureido diamine).

Examples of useful chain terminators include aminoalcohols, like ethanolamine, propanolamine, butanolamine, N-methylethanolamine, N-methyl-isopropanolamine, taurine and isethionic acid.

HEAT ACTIVATION AND GREEN STRENGTH

In heat activation process, the polyurethane dispersion adhesive is applied to the substrate and after complete evaporation of water the layer of adhesive applied is converted into an adhesive state by the action of heat. Good adhesives should exhibit low heat activation temperature and high green strength.

Generally, polyurethane adhesive having high crystallization rate should have low heat activation temperature and high green strength. U.S.Pat. 4,870,129 discloses that polyurethane dispersions based on HDI/IPDI exhibited low activating temperature and high heat resistance.

Unexpectedly, it has been found that polyurethane dispersions of the invention based on mixtures of HDI with other diisocyanates do not always have low activating temperature and high heat resistance. Heat activation temperature and green strength not only depend on crystallization rate, but also depend on molecular weight of polyurethane. In this invention, it has been found that polyurethane dispersions based on molar ratios* of HDI/TMXDI greater than 2/1 have high a crystallization rate, but have much different heat activating temperature and green strength. The results are shown in Table 3 for several compositions.

*In terms of wt, the molar ratio is:

HDI/TMXDI

$$2/1 \text{ (molar ratio)} = (2/84)/(1/122) \text{ (weight ratio)} = 3/1 \text{ (weight ratio)}.$$

Table 3. Crystallization Rate and Heat Activation

PUD Samples	#2	#36	#24	#37	#7	#44	#48	#8
Cry Rate (%)	0	54	56	60	65	66	75	76
Heat Activation (T-peel, Kg)								
125°F	1.3	0.3	0.3	0.4	0	0.4	5.9	0
150°F	3.5	0.2	0.3	0.4	0	3.3	7.7	0
175°F	4.8	0.4	0.4	2.2	0	9.3	11.8	0
200°F	6.2	0.3	0.4	5.3	0	10.5	11.9	0
Film Brittle*	3	4	4	3	5	2	1	5

* Film brittle: 1------------------>5

Minor Serious

Table 4. Compositions for samples in Table 3

PUD Samples	HDI/TMXDI (Mol %)	EDA/EA (Mol %)	Cry. Rate (%)	Film Brittle
#2	0/100	50/50	0	3
#24	67/33	50/50	54	3
#37	67/33	EA/Taurine	56	4
#7	67/33	0/100	65	5
#44	83/17	100/0	66	2
#48	83/17	80/20	75	1
#8	67/33	50/50	76	5

In view of the results shown above, it can be seen that the present invention provides aqueous polyurethane dispersions which have low heat activating temperature and high heat resistance based on HDI and its

mixture with other diisocyanate (crystallization rate), and EDA and its mixtures with chain terminators (crystallization rate and molecular weight).

Surprisingly, it was found that carboxylated polyurethane prepolymers with high crystallization rate and low heat activation temperature based on HDI or HDI mixture with other diisocyanate, polyester polyol and DMPA cannot be dispersed into water. A large particle size dispersion with precipitation always occurs.

On the other hand, when sulfonated polyurethane dispersions of the invention with high crystallization rate and low heat activation temperature were prepared (sulfonic acid is a stronger acid in comparison with carboxylic acid) the dispersions were found to have higher solubility in water in comparison with carboxylic acid based dispersions.

STABILITY AT LOW PH

Usually cationic and nonionic polyurethane dispersions have low pH (less than 7) stability, and anionic polyurethane dispersions are stable only at higher pH (greater than 7).

U.S.Pat. 4,870,129 discloses that sulfonated polyurethane dispersions can be stable at a pH of 5-7. A sodium salt of N-(-2 aminoethyl)-2-aminoethane sulphonic acid (AAS salt) was used as a chain extender to prepare the sulfonated polyurethane dispersions. A prepolymer containing sulfonate groups could not be prepared by this process. In addition, a large quantity of acetone was used to dilute the non-sulfonated prepolymer before adding the sulfonate diamine chain extender due to the high reactivity of the sulfonate diamine with diisocyanate.

Another U.S.Pat. 4,108,814 uses sulfonate diols (sulfonated polyether polyols) to prepare sulfonated polyurethane dispersions. These sulfonate diols were used to prepare prepolymers containing sulfonate groups, but these sulfonate diols contain ether bonds which should decrease the

crystallization of the resulting polyurethane dispersions.

In the present invention, however, new sulfonated polyester polyols were used to synthesize sulfonated aqueous polyurethane dispersions. Sulfonated polyester polyols were prepared from diacids, diols and sulfonate diacids and/or sulfonate diols. Aromatic and aliphatic sulfonate diacids and diols were used, and comprised 1-10% content of the resulting sulfonated polyester polyols.

Preferred sulfonated polyester polyols have melting points between 30° C and 80° C, most preferred between 40° C and 60° C. Especially preferred are sulfonated polyester polyols prepared by reacting sulfonate diacids or diols with short chain diols and short chain diacids or derivatives of diacids.

Examples of useful diols include ethylene glycol or condensates of ethyleneglycols, butanediol, butenediol, propanediol, neopentylglycol, hexanediol, 1,4-cyclohexane dimethanol, 1,2-propylene glycol and 2-methyl-1,3-propanediol.

Examples of useful diacids include adipic, azelaic, succinic, suberic acids, and phthalic acid.

Examples of useful sulfonate diacids and diols include sulfoisophthalic acid (and sodium salt), sulfossucinic acid (and sodium salts), 1,4-dihydroxybutane sulfonic acid (and sodium salt) and succinaldehyde disodium bisulfite.

Examples of commercially available sulfonated polyester polyols that are useful in the compositions of the invention are the "Rucoflex XS" series made by Ruco Polymer Corporation for H.B. Fuller. Rucoflex XS-5483-55 and Rucoflex XS-5536-60 are sulfonated polyester polyols based on 5-sulfoisophthalic acid monosodium salt (4 wt.% in XS-5483-55, and 6 wt.% in XS-5536-60), 1,6--hexanediol and adipic acid. See Table 5 below. 5-sulfoisophthalic acid monosodium salt is a cheaper key raw material for

preparing aqueous sulfonated polyurethane dispersions compared with the sodium salt of N-(2-aminoethyl)-2-aminoethane sulfonic acid as used in U.S. Patent 4,870,129. It contains an aromatic ring which will increase the heat resistance of the final resulting sulfonated polyurethane adhesives.

Table 5. Composition of Rucoflex SX-5484-55 and SX-5536-60

Rucoflex	adipic acid and 1,6-hexane diol	5-sulfoisophthalic acid monosodium salt
XS-5483-55	95%	4%
XS-5536-60	94%	6%

In accordance with this invention, the sulfonated polyester polyol selected was reacted with HDI or mixture of HDI with other diisocyanate at 70-90°C for 2-7 hours to prepare a prepolymer containing sulfonate groups. The prepolymer was dispersed into water, finally chain extended by EDA for example and/or chain terminators (e.g. EA).

Surprisingly, the reaction between the sulfonated polyester polyol and HDI (or mixture of HDI and other diisocyanate) was found to be quite rapid. The reaction was carried out at 70-80°C just for 3-10 minutes, and the reactant became a semi-solid or even a solid, which was difficult to dissolve into acetone.

Therefore, an acetone process was used to prepare the sulfonate containing prepolymer. The sulfonated polyester polyol was dehydrated in a vacuum at 100°C. Acetone was added to dissolve it at 70-80°C, and HDI and other diisocyanate (e.g. TMXDI) were then added. The reaction was carried at 80-90°C for 3-5 hours. After dispersing and chain extension, the acetone was then immediately distilled off. About half the amount of acetone used in U.S. Pat. 4,870,129 was used in this process.

The resulting sulfonated aqueous polyurethane dispersions possess stability at a low pH (5-7), in addition to high crystallization rate and low heat activation temperature. They have good compatibility with other water-based polymers (e.g. vinyl acetate emulsion), and crosslinker (e.g. Bayer/Miles' Desmodour DA). The resulting adhesives exhibit high heat resistance.

EXAMPLES

The invention is further illustrated, but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

Determination of Crystallization Rate

DSC is used to measure the crystallization rate. The film samples made from aqueous polyurethane dispersion are heated from -40 to 140°C at 10°C/minute. The resulting thermographies are "first run". The samples are then quench cooled and reheated at 10°C/minute to produce the thermographies are "second run".

Crystallization rate = DSC second run melting heat/ DSC first run melting heat. The results are shown in Table 4.

Heat Activation Testing

Drawdown polyurethane dispersion on a 10 mil clear PVC (polyvinyl chloride film from Laird Plastics) with a #28 mylar rod. Dry to touch and cut into lx6 inch strips. Seal the strips to uncoated 10 mil clear PVC using a Sentinal Heat Sealer at 50 psi nip pressure with a 30 second dwell time. Begin sealing at 125°F, increasing the temperature 25°F increments to 200°F. Allow laminates to age 15 minutes and determine peel

strength at 12 inches per minute on an Intelect 500. The results are shown in Table 6 below for the following Examples.

Example 1

229 g. Rucoflex XS-5483-55 (a sulfonated polyester polyol based on 5-sulfoisophthalic acid monosodium salt, adipic acid and 1,6-hexanediol, OH number 49.0) is dried in vacuo at 100°C. and then dissolved into 250 ml. acetone at 70-80°C. 21 g. 1,6-hexane-diisocyanate (HDI) and 6.1 g. tetramethylxylylene diisocyanate (TMXDI) are added, whereupon the temperature is maintained at about 85° C. for 5 hours and then cooled to about 50°C. At this temperature, the prepolymer is dispersed by adding 389 g. water, and then chain extended by adding 2.4 g. ethylenediamine (EDA) and 1.22 g. ethanolamine (EA). The acetone is then immediately distilled off.

A finely divided dispersion having a solids content of 40.7%, viscosity of 115 cps, particle size of 226 nm and a pH of 11.2 is obtained.

Example 2

343.5 g. Rucoflex XS-5483-55 is dried in vacuo at 100°C. and then 250 ml acetone, 30.24 g. HDI and 0.18 g. T-12 (dibutyltin dilaurate) are added into it at 70-80°C, whereupon the temperature is maintained at 80°C. for 2 hours. 10.98 g. TMXDI and 5.02 g. DMPA (dimethylolpropionic acid) is added, keep the temperature at 85°C. for another 3 hours. During the reacting, additional 300 ml acetone is added to control the viscosity of the reactant. The temperature is cooled to about 50°C, 600 g. water is added to disperse the prepolymer, 5 minutes later 2.25 g. EDA (in 30 g. acetone) is added. The acetone is then immediately distilled off.

A finely divided dispersion having a solids content of 39.3%, viscosity of 50 cps, and a pH of 6.41 is obtained.

Example 3

229 g. Rucoflex XS-5483-55 is dried in vacuo at 100°C. and then 0.09 g. T-12, 250 ml acetone and 21.0 g. HDI are added into it at 80°C. After maintaining at 80°C. for 2 hours, 6.1 g. TMXDI and 150 ml acetone are added, and keep the temperature at 85-90°C for another 3 hours. The temperature is cooled to about 50°C, 0.61 EA (ethanolamine) and 339 g. water first and then 2.7 g. EDA are added into the prepolymer acetone solution. The acetone is then immediately distilled off.

A finely divided dispersion having a solids content of 40.14%, viscosity of 420 cps and a pH of 11.5 is obtained.

Example 4

229 g. Rucoflex XS-5483-55 is dried in vacuo at 100°C. and then 0.09 g. T-12, 1.0 g. DMPA, 22.58 g. HDI and 250 ml acetone are added at 80°C. After maintaining at 80°C for 2 hours, 6.56 g. TMXDI is added, and keep at 85-90°C for another 3 hours. The temperature is cooled to about 50°C, 393.5 g. water, 1.64 g. EA and 0.61 g. EDA (in 30 g. acetone) are added. The viscosity of the resulting dispersion is too high, additional 50 g. water is added. The acetone is then immediately distilled off.

A finely divided dispersion having a solids contents of 35.16%, viscosity of 95 cps, particle size of 154 nm and a pH of 7.6 is obtained

Example 5

229 g. Rucoflex XS-5483-55 is dried in vacuo at 100°C, and then 1.34 g. DMPA, 0.09 g. T-12, 23.1 g. HDI, 2.69 g. TMXDI and 250 ml acetone are added at 85°C. After maintaining at 85°C for 5 hours, the temperature is cooled to about 50°C, then 387 g. water, 0.7 g. EA and 1.62 g. EDA (in 50 g. water) are added into the prepolymer. The acetone is then immediately distilled off.

A finely divided dispersion having a solids contents of 35.5%, viscosity of 515 cps, and a pH of 8.09 is obtained.

Example 6

229 g. Rucoflex XS-5483-55 is dried in vacuo at 100°C and then 1.34 g. DMPA, 23.1 g. HDI, 2.69 g. TMXDI, 0.09 g. T-12 and 250 ml acetone are added at 85°C. After maintaining at 85°C for 5 hours, the temperature is cooled to about 50°C, then 386.98 g. water and 1.85 g. EDA are added into the prepolymer. The viscosity of the resulting dispersion is too high, additional 100 q. water is added. The acetone is then immediately distilled off.

A finely divided dispersion having a solids content of 36.32%, viscosity of 104 cps, particle size of 117 nm and a pH of 7.45 is obtained.

Example 7

229 g. Rucoflex XS-5483-55 is dried in vacuo at 100°C, and then 0.09 g. T-12, 21.0 g. HDI and 450 ml acetone are added at 80°C. After maintaining at 80°C for 2 hours, 9.76 g. TMXDI is added, and the reaction is carried out at 85-90°C for another 3 hours. After the temperature is cooled to about 50°C, 397 g. water, 2.38 g. EA and 2.73 g. EDA (in 30 g. acetone and 20 g. water) are added into the prepolymer. The acetone is then immediately distilled off.

A finely divided dispersion having a solids content of 35.75%, viscosity of 300 cps, particle size 198 nm and a pH of 10.95 is obtained.

Example 8

114.5 g. Rucoflex XS-5483-55 and 50 g. Rucoflex S-102-55 (1-6 butanediol adipate polyester polyol, OH No. 55) and 6.7 g. DMPA are dried in vacuo at 100°C, then 17.64 g. HDI, 9.6 g. TEA (triethylamine) and 50 ml

acetone are added at 75°C. After maintaining at 80°C for 2 hours, 12.2 g. TMXDI is added, and the reaction is carried out at 85-90°C for another 3 hours. The temperature is cooled to about 50°C, 100 ml acetone is added, then 568.7 g. water and 1.8 g. EDA (in 35 ml acetone) are added into the prepolymer. After distilling acetone off, a finely divided dispersion is obtained.

Example 9

200 g. Rucoflex S-102-55 (Ruco's polyester polyol based on butanediol adipate, OH number 55.0) is dried in vacuo at 100°C, and then 20.1 g. DMPA, 34.8 g. HDI and 14.4 TEA are added at 70°C. After maintaining at 80°C for 2 hours, 24.4 g.TMXDI is added, the reaction is carried out at 90-100°C for another 3 hours. The temperature is cooled to 70°C, 150 ml acetone is added, and then 6.25 g. taurine and 4.58 g. EA in 790 g. water are added into the prepolymer. After distilling acetone off, a finely divided dispersion is obtained.

Example 10

181 g. Rucoflex XS-5536-60 (a sulfonated polyester polyol based on 5-sufoisophthalic acid monosodium salt (6%), adipic acid and 1,6-hexanediiol, OH number 61.9) is dried in vacuo at 100° C, and then 1.0 g. DMPA, 0.08 g. T-12, 22.58 b. HDI and 200 ml acetone are added at 80° C. After maintaining at 80° C for 2 hours, 6.50 g. TMXDI is added, the reaction is carried out at 85-90° C for another 3 hours. After the temperature is cooled to about 50° C, 422 g. water with 1.68 g. EA and 1.61 g. EDA are added into the prepolymer. The acetone is then immediately distilled off.

A finely divided dispersion having a solids content of 26.10%, viscosity of 60 cps, particle size 41 nm and a pH of 7.63 is obtained.

Table 6

Example	HDI/TMXDI (Mol %)	EDA/EA (Mol %)	Cry. Rate (%)	T-Peel (Kg) Activating at (°F)			
				125	150	175	200
1	83/17	83/20	75.2	5.9	7.7	11.8	11.9
2	80/20	100/0	67.2	1.5	6.9	10.1	10.5
3	83/17	90/10	71.6	2.3	6.0	10.1	12.6
4	83/17	50/50	65.8	3.8	6.8	11.9	13.5
5	93/7	70/30	65.3	1.0	6.3	----	10.9
6	93/7	100/0	65.0	1.7	5.2	7.2	----
7	76/24	70/30	78.9	4.3	8.7	12.8	12.4
8	68/32	100/0	56.9	3.4	4.5	8.0	7.7
9	60/40	Taurine/EA	56.0	0.3	0.3	0.4	0.4
10	83/17	50/50	61.0	1.6	2.2	3.6	4.2

While this invention may be embodied in many different forms, there are described in detail herein specific preferred embodiments of the invention. This description is an exemplification of the principles of the invention and is not intended to limit the invention to the particular embodiments illustrated.

The above Examples and disclosure are intended to be illustrative and not exhaustive. These examples and description will suggest many variations and alternatives to one of ordinary skill in this art. All these alternatives and variations are intended to be included within the scope of the attached claims. Those familiar with the art may recognize other equivalents to the specific embodiments described herein which equivalents are also intended to be encompassed by the claims attached hereto.

WHAT IS CLAIMED IS AS FOLLOWS:

1. A stable aqueous dispersion of anionic polyurethane wherein the polyurethane comprises the reaction product of A and B as identified below:

A. an isocyanate terminated sulfonated prepolymer prepared in the presence of acetone by reacting components (i) and (ii) wherein

(i) is selected from the group consisting of
a sulfonated polyester polyol,
its mixture with dimethylol propionic acid (DMPA),
its mixture with polyester polyol and DMPA,
its mixture with polyether polyol and DMPA,
its mixture with polyester- and polyether-polyol, and DMPA
and mixtures thereof

(ii) is selected from the group consisting of
hexamethylene diisocyanate (HDI),
HDI mixed with trimethylxylyene diisocyanate (TMXDI),
HDI mixed with another aromatic diisocyanate,
HDI mixed with another aliphatic diisocyanate,
and mixtures thereof

to form a component which is then reacted with B, optionally in the presence of triethylamine if the component is not in a salt form, in the presence of water wherein

B. is selected from the group consisting of
an aliphatic diamine,
a cycloaliphatic diamine,
an aromatic diamine,
an aminoalcohol,
ethylene diamine (EDA),
EDA mixed with ethanolamine,

EDA mixed with taurine,

EDA mixed with isethionic acid,

EDA mixed with N-isodecyloxypropyl-1,3-diaminopropane

EDA mixed with ureido diamine,

and mixtures thereof.

2. The aqueous dispersion according to Claim 1 wherein the acetone is removed after the dispersion if formed.

3. A dispersion according to Claim 1 wherein the sulfonated polyester polyol is selected from one of the groups consisting of diacids, diols, sulfonate diacids, sulfonate diols and mixtures thereof.

4. The dispersion according to Claim 3 wherein the diacids and diols are selected from the group consisting of aromatic and aliphatics.

5. The dispersion according to Claim 4 wherein the diacids are selected from the group consisting of adipic, azelaic, succinic, suberic and phthalic acids.

6. The dispersion according to Claim 4 wherein the diols are selected from the group consisting of ethyleneglycol, condensates of ethyleneglycols, butanediol, butenediol, propanediol, neopentylglycol, hexanediol, 1,4-cyclohexane dimethanol, 1,2-propylene glycol and 2-methyl-1,3-propanediol.

7. The dispersion according to Claim 3 wherein the sulfonate diacids and sulfonate diols are sulfoisophthalic acid, sulfosuccinic acid, 1,4-dihydroxybutane sulfonic acid and succinaldehyde disodium bisulfite.

8. The sulfonated polyester polyol is based on 5-sulfoisophthalic acid monosodium salt, 1,6-hexanediol and adipic acid.

9. The dispersion according to Claim 8 wherein the sulfonated polyester polyol has a molecular weight in the range of about 500 to 10,000 and a melting temperature in the range of about 10 to 100°C.

10. The dispersion according to Claim 9 wherein the molecular

weight range is about 1,000 to 4,000 and the melting temperature is about 40 to 60° C.

11. The dispersion of Claim 1 wherein the ratio of HDI mixed with any of the second mentioned diisocyanates ranges from 100/0 to 0/100 by weight.

12. The dispersion of Claim 11 wherein the ratio ranges from 100/0 to 50/50 by weight.

13. The dispersion of Claim 1 including chain extender/chain terminators and wherein the ratio of chain extender to chain terminator ranges from 100/0 to 0/100 by weight.

14. The dispersion of Claim 13 wherein the ratio ranges from about 50/50 to about 100/0.

15. A water dispersible polyurethane prepolymer composition comprising the reaction product of components A and B,
component A being selected from the group consisting of:

a sulfonated polyester polyol, a sulfonated polyester polyol mixed with dimethylol propionic acid (DMPA), a sulfonated polyester polyol mixed with another polyester polyol and DMPA, a sulfonated polyester polyol mixed with a polyester polyol and DMPA, and a sulfonated polyester polyol mixed with another polyester polyether polyol and DMPA;

component B being selected from the group consisting of:

hexamethylene diisocyanate (HDI), HDI mixed with tetramethylxylyene (TMXDI), HDI mixed with an aromatic diisocyanate, HDI mixed with another aliphatic diisocyanate, and mixtures thereof.

16. The prepolymer of Claim 15 wherein the aromatic diisocyanate is toluene diisocyanate (TDI).

17. The prepolymer of Claim 15 wherein the aromatic diisocyanate

is 4,4' diphenylmethane diisocyanate (MDI).

18. The prepolymer of Claim 15 wherein the aliphatic diisocyanate is isophone diisocyanate (IPDI).

19. The prepolymer of Claim 15 wherein the aliphatic diisocyanate is dicyclohexylmethane 4,4-diisocyanate ($H_{12}MDI$).

20. The dispersion of Claim 15 wherein the ratio of HDI mixed with any of the second mentioned diisocyanates ranges from 100/0 to 0/100 by weight.

21. The dispersion of Claim 15 wherein the ratio ranges from 100/0 to 50/50 by weight.

22. The dispersion of Claim 15 wherein the ratio of chain extender to chain terminator ranges from 100/0 to 0/100 by weight.

23. The dispersion of Claim 15 wherein the ratio ranges from about 50/50 to about 100/0.

24. An aqueous polyurethane dispersion wherein the polyurethane comprises the reaction product of:

a first reactant selected from the group consisting of:

a sulfonated polyester polyol, a sulfonated polyester polyol mixed with dimethylol propionic acid (DMPA), a sulfonated polyester polyol mixed with another polyester polyol and DMPA and a sulfonated polyester polyol mixed with another polyester polyether polyol and DMPA, and mixtures thereof;

the first reactant being reacted with a component selected from the group consisting of:

hexamethylene diisocyanate (HDI), HDI mixed with tetramethylxylyene diisocyanate (TMXDI), HDI mixed with an aromatic diisocyanate, HDI mixed with another aliphatic diisocyanate, and mixtures thereof,

to form a prepolymer,

which in aqueous dispersion is caused to undergo further reaction with a component selected from the group consisting of chain extenders, chain terminators and both chain extenders and chain terminators.

25. The dispersion of Claim 24 wherein the ratio of HDI mixed with any of the second mentioned diisocyanates ranges from 100/0 to 0/100 by weight.

26. The dispersion of Claim 24 wherein the ratio ranges from 100/0 to 50/50 by weight.

27. The dispersion of Claim 24 wherein the ratio of chain extender to chain terminator ranges from 100/0 to 0/100 by weight.

28. The dispersion of Claim 24 wherein the ratio ranges from about 50/50 to about 100/0.

29. An aqueous anionic polyurethane dispersion based on the reaction product of:

(a) a polyol selected from the group consisting of a sulfonated polyester polyol or a polyol mixture including a sulfonated polyester polyol, and

(b) a diisocyanate mixture including hexamethyylene diisocyanate (HDI) mixed with a diisocyanate selected from the group consisting of tetaramethylxylylene diisocyanate (TMXDI), aromatic diisocyanate and aliphatic diisocyanate to form a prepolymer which is dispersed in water and caused to undergo either chain extension, chain termination or both.

30. The dispersion of Claim 29 wherein the chain extender/terminator is selected from the group consisting of aliphatic diamine, cycloaliphatic diamines, aromatic diamines, aminoalcohols and mixtures thereof.

31. The dispersion of Claim 29 wherein the ratio of HDI mixed with

any of the second mentioned diisocyanates ranges from 100/0 to 0/100 by weight.

32. The dispersion of claim 29 wherein the ratio ranges from 100/0 to 50/50 by weight.

33. The dispersion of Claim 29 wherein the ratio of chain extender to chain terminator ranges from 100/0 to 0/100 by weight.

34. The dispersion of Claim 29 wherein the ratio ranges from 50/50 to about 100/0.

35. An aqueous anionic polyurethane dispersion based on the reaction product of:

(a) a polyol selected from the group consisting of a sulfonated polyester polyol or a mixture thereof with components selected from the further group consisting of dimethylol propionic acid (DMPA), polyester polyols and DMPA, polyether polyols and DMPA, and mixtures thereof, and

(b) hexamethylene diisocyanate (HDI) and its mixture with another diisocyanate selected from the group consisting of (TMXDI) tetramethylxylylene diisocyanate, an aromatic diisocyanate or another aliphatic diisocyanate to form a prepolymer which is chain extended and/or chain terminated in forming the dispersion.

36. The dispersion of Claim 35 wherein the aromatic diisocyanate is selected from the group consisting of TDI, MDI and mixtures thereof.

37. The dispersion of Claim 35 wherein the another aliphatic diisocyanate is selected from the group consisting of IPDI, H_{12}MDI and mixtures thereof.

38. The dispersion according to Claim 35 wherein the chain extender and chain terminator is comprised of ethylene diamine.

39. The dispersion of Claim 35 wherein the ratio of HDI mixed with any of the second mentioned diisocyanates ranges from 100/0 to 0/100 by weight.

40. The dispersion of Claim 35 wherein the ratio ranges from 100/0 to 50/50 by weight.

41. The dispersion of Claim 35 wherein the ratio of chain extender to chain terminator ranges from 100/0 to 0/100 by weight.

42. The dispersion of Claim 35 wherein the ratio ranges from about 50/50 to about 100/0.

43. An aqueous anionic polyurethane dispersion formed from a prepolymer comprised of the reaction product of A and B as defined below wherein:

A is selected from the group consisting of at least one sulfonated polyester polyol, a mixture of at least one sulfonated polyester polyol with dimethylol propionic acid (DMPA), a mixture of at least one sulfonated polyester polyol with polyester polyol and DMPA, and a mixture of at least one sulfonated polyester polyol with polyether polyol and DMPA and mixtures thereof;

B is selected from the group consisting of hexamethylene diisocyanate (HDI), a mixture of HDI with tetramethylxylylene diisocyanate (TMXDI), a mixture of HDI with an aromatic diisocyanate, a mixture of HDI with an aliphatic diisocyanate; and mixtures thereof,

and the prepolymer is dispersed in water with a component C, and wherein

C is a chain modifier selected from the group consisting of ethylenediamine (EDA), a mixture of EDA with taurine, a mixture of ethanolamine (EA) with isethionic acid or a mixture of EDA with N-isodecyloxy propyl-1,3-diaminopropane, a mixture of EDA with Ureido diamine (imidazolidinone diamine).

44. The dispersion according to Claim 43 wherein the taurine is in salt form

45. The dispersion according to Claim 43 wherein the isethionic acid is in salt form.

46. The aqueous anionic polyurethane dispersion of claim 43 wherein said aromatic diisocyanate is TDI or MDI.

47. The aqueous anionic polyurethane dispersion of claim 43 wherein said aliphatic diisocyanate is IPDI and $H_{12}MDI$.

48. The dispersion of Claim 43 wherein the ratio of HDI mixed with any of the second mentioned diisocyanates ranges from 100/0 to 0/100 by weight.

49. The dispersion of Claim 43 wherein the ratio ranges from 100/0 to 50/50 by weight.

50. The dispersion of Claim 43 wherein the ratio of chain extender to chain terminator ranges from 100/0 to 0/100 by weight.

51. The dispersion of Claim 43 wherein the ratio ranges from about 50/50 to about 100/0.

52. A method of preparing a stable aqueous dispersion of an ionic polyurethane comprising the steps of:

(a) preparing an isocyanate terminated sulfonated prepolymer in the presence of acetone from:

(i) a polyol component selected from the group consisting of a sulfonated polyester polyol; a sulfonated polyester polyol mixed with dimethylol propionic acid (DMPA); a sulfonated polyester polyol mixed with a polyester polyol and DMPA; a sulfonated polyester polyol mixed with a polyether polyol and DMPA; and a sulfonated polyester polyol mixed with a polyester polyether-polyol and DMPA;

(ii) an isocyanate component selected from the group consisting of hexamethylene diisocyanate (HDI), HDI mixed with tetramethylxylene diisocyanate (TMXDI), HDI mixed with an aromatic diisocyanate and HDI mixed with another aliphatic diisocyanate, and

(b) combining the prepolymer in water with either a chain modifier selected from the group consisting of alkylene diamines,

ethylenediamine (EDA), and a mixture of EDA with a compound from the further group consisting of ethanolamine, taurine, taurine in salt form, isethionic acid, the salt of isethionic acid, N-isodecyloxypropyl-1,3-diaminopropane (DA-14), and ureido diamine.

53. The method of Claim 52 wherein aromatic diisocyanate is selected from the group consisting of TDI and MDI.

54. The method of Claim 52 wherein the aliphatic diisocyanate is selected from the group consisting of IPDI, and $H_{12}MDI$.

55. The method of Claim 52 wherein the sulfonated polyester polyols are prepared from diacids, diols, sulfonate diacids and/or sulfonate diols.

56. The method of Claim 55 wherein the sulfonate diacids and diols are aromatic and aliphatic.

57. The method of Claim 52 wherein the sulfonated polyester polyol is prepared from 5-sulfoisophthalic acid monosodium salt, 1,6-hexanediol and adipic acid.

58. The method of Claim 52 wherein the sulfonated polyester polyols have molecular weight of about 500-10000, and a melting point of about 10-100°C.

59. The method of Claim 52 wherein the sulfonated polyester polyols have molecular weight of about 1000-4000 and a melting point of about 40-60°C.

60. The method of Claim 52 wherein

(a) the polyol component is a sulfonated polyester polyol;

(b) the diisocyanate component is selected from the group consisting of HDI and mixtures of HDI;

(c) the polyol is reacted with the diisocyanate component at a temperature of about 70-90°C for about 2-7 hours to prepare a prepolymer containing sulfonate groups;

(d) the prepolymer is dispersed into water and combined with chain extender and\or chain terminator.

61. The method of Claim 52 wherein the polyol and diisocyanate are reacted at a temperature of about 70-80°C for about 3-10 minutes, and the resulting high viscosity reactant is dissolved in acetone for further reacting the diisocyanate with the polyol.

62. The method of Claim 61 wherein the polyol is dissolved in the acetone prior to reacting with the diisocyanate.

63. The method of Claim 52 wherein

(a) the sulfonated polyester polyol is dehydrated in a vacuum at about 100°C and dissolved in acetone at a temperature of about 70-80°C;

(b) the diisocyanate is added, after which the reaction is carried out at about 80-90°C for about 3-5 hours.

(c) the prepolymer is dispersed into water and combined with either a chain extender, a chain terminator or both.

(d) the acetone is distilled off.

64. The sulfonated aqueous polyurethane dispersion according to Claim 63 used in adhesives.

65. The sulfonated aqueous polyurethane dispersion according to Claim 63 in combination with other water-based polymers and crosslinkers.

66. The method of Claim 52 wherein the ratio of HDI mixed with any of the second mentioned diisocyanates ranges from 100/0 to 0/100 by weight.

67. The method of Claim 52 wherein the ratio ranges from 100/0 to 50/50 by weight.

68. The method of Claim 52 wherein the ratio of chain extender to chain terminator ranges from 100/0 to 0/100 by weight.

69. The method of Claim 52 wherein the ratio ranges from about 50/50 to about 100/0.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/06406

A. CLASSIFICATION OF SUBJECT MATTER
IPC(5) :C08G 18/46, 18/73; C08K 5/42; C08L 75/06
US CL :524/591, 840; 528/67, 71, 80, 83
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/591, 840; 528/67, 71, 80, 83

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,108,814 (REIFF ET AL) 22 August 1978.	1-69
A	US, A, 4,385,137 (LORENZ ET AL) 24 May 1983.	1-69
Y	US, A, 4,870,129 (HENNING ET AL) 26 September 1989, abstract, column 2, lines 27+, column 3, lines 18+, column 4, column 5, column 6, lines 1-56.	1-69
A	US, A, 5,001,189 (FOCK ET AL) 19 March 1991.	1-69

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be part of particular relevance
"E" earlier document published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 AUGUST 1994	15 SEP 1994

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/06406

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,E	US, A, 5,334,690 (SCHAFHEUTLE ET AL) 02 August 1994, abstract, column 1, lines 48+, column 2, lines 27+, column 3, lines 61+, column 4, lines 12+, column 5, column 6, lines 1-26.	1-69